

Preparation and characterization of spray deposited CoS thin films

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Abstract : Thin films of CoS have been deposited onto glass substrates by a spray pyrolysis technique using thiourea as a sulphur source and cobalt sulphate as a metal ion source. The structural, optical and electrical properties of these films have been studied. It has been found that films are microcrystalline. The optical absorption studies show that CoS is a direct bandgap material having bandgap energy to be 0.97 eV and electrical resistivity is of the order of $10^4 \Omega\text{-cm}$ at room temperature (300 K). Thermoelectric power measurements (TEP) reveals that the CoS is a p-type semiconductor.

Keywords : CoS thin films, optical absorption, electrical resistivity

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1. Introduction

Metal chalcogenide thin films have been studied over last 25 years in view of their potential applications. CoS is one of them having bandgap energy equal to 0.90 eV. It has potential applications in IR detector, optoelectronic devices, decorative coatings, solar selective coatings and as a storage electrode in photoelectrochemical storage devices [1,2]. CoS films have been deposited by Lokhande [3] using chemical bath deposition technique in acidic medium and reported that the films are polycrystalline with bandgap energy of 0.9 eV. Basu and Pramanik [4] prepared CoS thin films by using chemical deposition (CBD) technique from alkaline thioacetamide (TAM) bath and films were polycrystalline. No attempt has been taken so far to prepare CoS film using spray pyrolysis method. The spray pyrolysis is a simple and economical method for deposition of chalcogenide films [5] and growth rate can be controlled through the parameters like spray rate, substrate temperature, nozzle frequency *etc.*

In the present study, CoS films have been prepared using spray pyrolysis technique. Preparative parameters like spray rate, deposition temperature, nozzle frequency, *etc* are optimized.

Characterization of the films has been carried out using X-ray diffraction (XRD), optical absorption, d.c. resistivity and thermoelectric power measurements.

2. Experimental details

The AR grade cobalt sulphate (CoSO_4) and thiourea [$\text{CS}(\text{NH}_2)_2$] are used for the preparation of CoS thin films. Double distilled water was used as a solvent. The CoS thin films were prepared by taking 0.1 M solutions of cobalt sulphate and thiourea in a Co : S ratio as 1 : 1. The mixed solution was then sprayed onto the glass substrates maintained at the optimized substrate temperature of 250°C . The spray rate was maintained to be 10 cc/min, the nozzle to substrate distance was 28 cm, and nozzle was moved back and forth over the substrates with a frequency of 0.30 Hz.

Characterization :

The thickness of the prepared thin film was determined using a relation

$$\rho_s = m/(A \cdot t), \quad (1)$$

where m is the mass of the thin film deposited onto the substrate, A is the area of the deposition film, t is the film thickness and ρ_s is the density of deposited material which is assumed to be the same as that of bulk material ($\rho_s = 4.88 \text{ g/cm}^3$ for CoS). The structural characterization of CoS thin films was carried out by analyzing X-ray diffraction patterns, obtained using Philips X-ray diffractometer model PW-1710 ($\lambda = 1.5405 \text{ \AA}$ for Cu-K α radiation). Optical absorption studies were carried out using a UV-VIS-NIR spectrophotometer (Hitachi model 330, Japan) in the wavelength range 900–2000 nm. To study electrical properties of CoS thin films, dark resistivity measurements were taken using a two point probe method in the temperature range 300 to 500 K. Silver paste was applied to provide ohmic contact with the CoS film [6]. Thermoelectric power measurement was carried out in the temperature range of 300 to 420 K.

3. Results and discussion

In the spray method, the starting materials required to form the desired compound are in the form of solutions, which are sprayed on the preheated substrates, resulting in the formation of thin films on the substrates. When the droplets of the above sprayed solution reach to the hot substrates, owing to pyrolytic decomposition of the solution, well adherent and red colored films of CoS are formed onto the substrates. The thickness of films was measured by a weight difference method and was found to be $0.83 \mu\text{m}$. The films are deposited at different substrate temperatures from 200 to 300°C . It is found that the films prepared at 250°C are uniform and well adherent to the substrate.

The XRD patterns of films were recorded in the range of diffracting angle 0 – 80° , as shown in Figure 1. Close inspection of the XRD pattern (by considering peak count and

background count) indicates the presence of (100), (211) planes of CoS material. Further it is seen that the CoS films are microcrystalline. The 'd' values of planes are calculated by

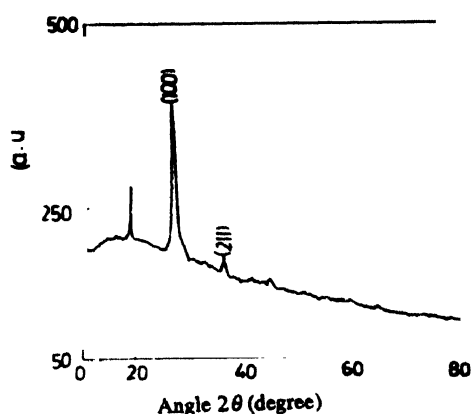


Figure 1. XRD pattern of CoS thin film.

assuming hexagonal structure and are compared with standard 'd' [7] values of CoS taken from ASTM diffraction data file and are presented in Table 1.

Table 1. Comparison of observed 'd' values with standard 'd' values of CoS films.

Calculated 'd' values	Standard 'd' values	Reflection planes
(1) 2.9190	2.93	100
(2) 1.084	1.083	211

The observed 'd' values are in good agreement with standard 'd' values confirming that the material of the films deposited is CoS.

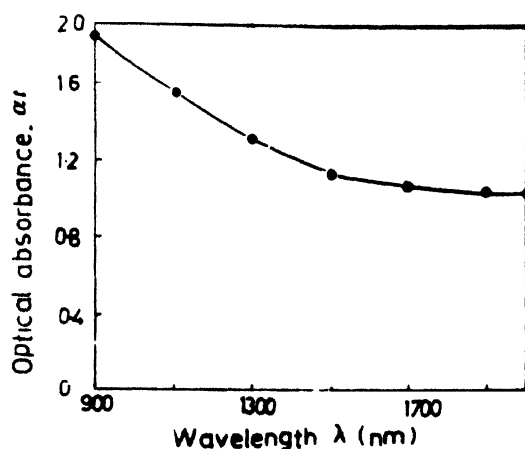


Figure 2. (a) Variation of the relative absorbance αt with wavelength λ for CoS thin films.

Optical absorption study of CoS films is carried out in the wavelength range 900–2000 nm. Figure 2(a) shows optical absorbance (αt) versus wavelength (nm). From calculation, absorption coefficient is found to be 10^4 cm^{-1} , supporting the presence of direct

bandgap [8]. Also the nature of transition (direct or indirect) involved can further be analyzed by considering the dependence of α on $h\nu$

$$\alpha \propto (h\nu - E_g)^{1/2}, \quad (2)$$

where E_g is the separation between the conduction and valence bands.

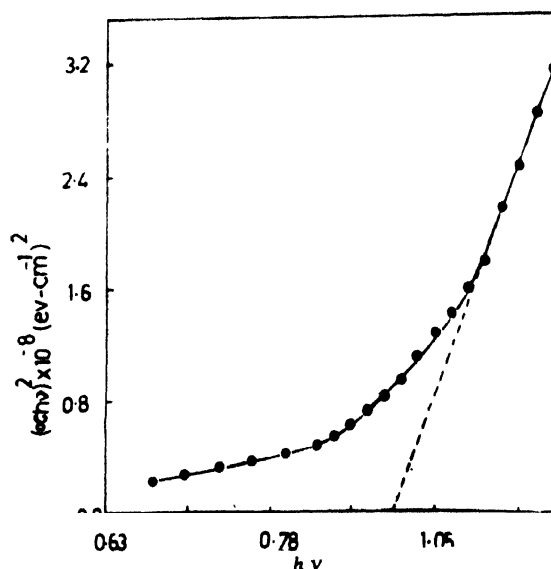


Figure 2. (b) Plot of $(\alpha h\nu)^2$ against $h\nu$ for CoS film.

Using the above data, the plot of $(\alpha h\nu)^2$ vs $h\nu$ is plotted. It is found that the plot is nonlinear indicating absence of indirect transition. In the present case, the plot of $(\alpha h\nu)^2$ vs $h\nu$ is linear (Figure 2(b)), indicating that the transition is a direct one. The extrapolation of the linear portion of such a plot to $\alpha = 0$ gives the bandgap energy, E_g to be 0.97 eV. The presence of a direct bandgap in CoS films has been reported with E_g equal to 0.90 eV [3]. The difference in the present case may be attributed to the different mechanism and deposition technique of film formation.

The variation of $\log \rho$ with $1/T$ is depicted in Figure 3, indicating the semiconducting nature of the prepared films. Non linear nature of the graph shows of many defect levels in the films. The dark resistivity is of the order of $10^4 \Omega\text{-cm}$. The electrical resistivity at room temperature is found to be $0.40 \times 10^4 \Omega\text{-cm}$. The activation was estimated using the relation,

$$\rho = \rho_0 \exp (E_a/KT) \quad (3)$$

The activation energy of CoS films is found to be 0.034 eV.

The thermoelectric power (TEP) measurements was carried out for CoS films in the temperature range of 300 to 420 K. Variation of thermoelectric power with rise in

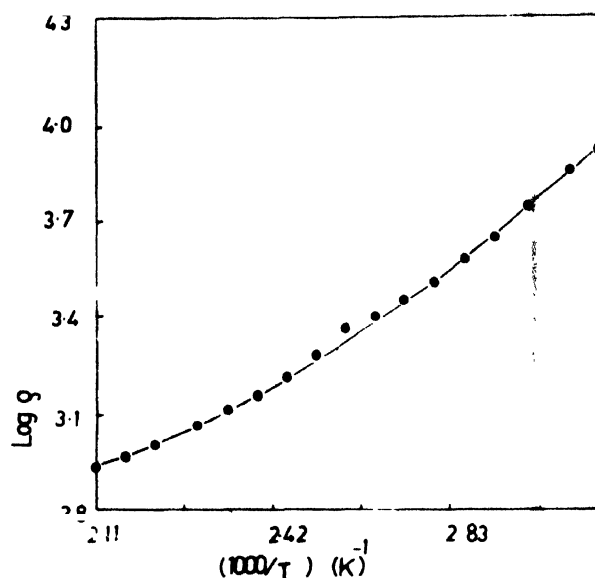


Figure 3. Variation $\log \rho$ with reciprocal of temperature for CoS film.

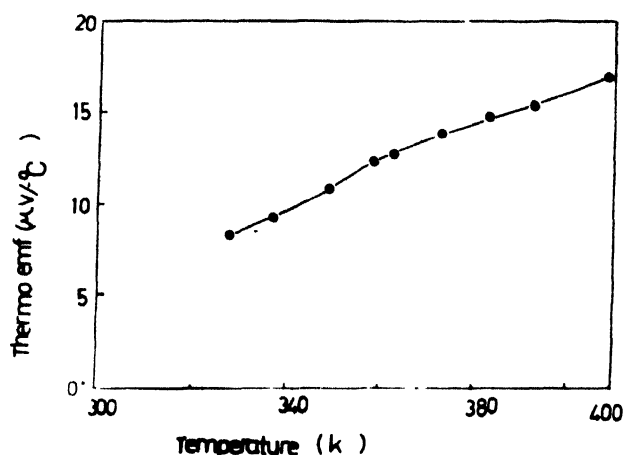


Figure 4. Variation of thermo emf with temperature for CoS film.

temperature is shown in Figure 4. TEP increases with rise in temperature. It was found that the polarity of thermally generated voltage at the hot end is negative indicating that CoS films are of p-type conductivity.

4. Conclusions

CoS films deposition is possible using spray pyrolysis technique. The films prepared at $250^{\circ}C$ are uniform as well as adherent to the substrate. The films are microcrystalline. The electrical resistivity of the films is found to be $0.40 \times 10^4 \Omega\text{-cm}$ at room temperature. The films deposited by spray pyrolysis show p-type conductivity.

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